Kinetic Studies on the Strictly Catalytic Acetylation of Mesitylene with Acetic Anhydride by HCl and Metal Chlorides in Acetic Acid

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On the acetylation of mesitylene (**1**, 0.5—1 mol dm^{-3}) with acetic anhydride (Ac_2O, 0.5—1.5 mol dm^{-3}) at 30—90 °C in acetic acid as solvent, $SbCl_5$, $FeCl_3$, $SnCl_4$, or $ZnCl_2$ (each of 0.02—0.2 mol dm^{-3}) under the co-catalytic effect of HCl (0—0.75 mol dm^{-3}) showed a continuous catalytic activity. The product was exclusively 2′,4′,6′-trimethylacetophenone for conversions of **1** in the range of 0—90%. The reaction was first order with respect to **1** and Ac_2O. The rate constants were proportional to 1—1.4th power of the concentration of the metal chloride. The apparent activation energy was 18.8 kcal mol^{-1} for all the catalysts. The catalytically active species are thought to be the conjugate acids from the metal chloride and HCl. Relative catalytic activities of the metal chlorides varied in parallel with their relative Lewis acid-strengths.

With a few exceptions,[1a,2] the past Friedel-Crafts acylations of aromatic hydrocarbons with acid halides, acid anhydrides, or acids required[3—7] more than equimolar amounts of metal halides (MX_n) to the acyl component, because the resulting ketone combined with MX_n to form a complex.[7,8] Although a recent patent suggests an acylation by a *catalytic amount* of $FeCl_3$, namely by 0.05—0.1 mol of $FeCl_3$ for each mol of acetyl chloride (AcCl),[2] the efforts to reduce the amount of the catalyst were concentrated on dissociating the complexes by means of elevating the reaction temperature beyond the boiling point of the starting hydrocarbons, and the yield of ketones was not high.

Catalytic amounts of strong inorganic oxoacids are known to catalyze continuously the acetylation of thiophene,[1b] furan,[1b] and anisole[9] with acetic anhydride (Ac_2O). In the case of anisole,[9] the addition of acetic acid (AcOH) made the reaction mild and it prevented the formation of resinous products. These results should be compared with conventional acylations[3,4,10b] which required 2—3 times the molar quantity of metal halides such as $AlCl_3$ to acid anhydrides. Solutions of $SnCl_4$ or $ZnCl_2$ in AcOH, without undergoing solvolysis, form complex acids with the solvent, *e.g.*, $H_2ZnCl_2(OAc)_2$.[10a] In the system of $ZnCl_2$–HCl–AcOH, an acid stronger than $HClO_4$, H_2ZnCl_4 arises.[11] A Brönsted acid (HY) such as HCl, H_2O, and AcOH often functions as a co-catalyst in the systems of MX_n in an aprotic solvent, where a conjugate acid HMX_nY with a strong ability of proton donation was thought to be the catalytically active species.[12—15]

Prior to the present study there has been neither a kinetic study of Friedel-Crafts acylation with anhydrides, nor a catalytic study of the acylation of an aromatic hydrocarbon with anhydrides. Recently the authors found a new acetylation of cyclic sesquiterpenes with Ac_2O in the presence of a *catalytic amount* of ZnO or Fe_2O_3, and HCl in AcOH as solvent.[16] This paper deals with the kinetic study of the acetylations of mesitylene (**1**) with Ac_2O in the presence of *catalytic amounts* of various metal chlorides (MCl_n) and HCl in AcOH as solvent.

Experimental

Catalysts. $ZnCl_2$ of a guaranteed reagent grade, $SnCl_4$ and $FeCl_3$ of a purity greater than 99 wt%, and $SbCl_5$ of an electronics grade were used as the catalysts without further purification.

Materials. **1** of a purity greater than 98.5 wt% (by GLC), and Ac_2O, AcCl, and AcOH of a guaranteed reagent grade were used without further purification. (In one particular case, 6 mol dm^{-3} HCl was used instead of AcCl, water contained in which was predicted to react quantitatively with Ac_2O to form AcOH.)

Procedure. The acylation was carried out under an atmosphere of dry N_2 in a 30 ml three-necked flask equipped with a condenser which was connected to a bubble column sealed with concd H_2SO_4. N_2 was introduced through a side arm and discharged through the condenser. The desired amounts of AcCl or 6 mol dm^{-3} HCl, Ac_2O, and **1** were weighed into a 20 ml-measuring flask, and AcOH was added to the mixture to make the total amount 20 ml at room temperature. The desired amount of a catalyst (MCl_n) was weighed quickly into the reaction flask and the above AcOH solution was added to it. Immediately, the mixture was stirred vigorously by a magnetic stirrer in a water bath with a thermostat. At each reaction time, *ca.* 1.5 ml sample of the reaction mixture was taken out, diluted with 25 ml of 20 wt% NaCl aqueous solution to stop the reaction, and extracted with 10 ml of diethyl ether. The water layer was extracted again with 10 ml of diethyl ether. Both extracts were then combined, washed with NaCl-saturated water and, after concentration, used for the GLC analysis. Occasionally the N_2 flow was stopped. Each time, no bubbles were found in the bubble column. This showed that any losses of HCl or AcCl from the reactor were not substantial. AcCl or HCl (0—0.75 mol dm^{-3}), 0.5—1 mol dm^{-3} of **1**, 0.35—1.35 mol dm^{-3} of Ac_2O, and 0.02—0.2 mol dm^{-3} of a catalyst were used. The reaction temperature was between 30 and 90 °C. The reference volume of the reaction mixture used to express the concentration of components was taken at 25 °C.

GLC Analysis. Quantitative analysis was done by means of an internal standard method, using a Shimadzu GC-6A apparatus on a 1 m×2 mmϕ column packed with 5 wt% of FFAP on Chromosorb W,AW-DMCS of 80—100 mesh. The column temperature was elevated from 80 to 250 °C by 10 °C min^{-1}, N_2 was used as the carrier at 40 ml min^{-1}, and the injection temperature was 230 °C. Cyclododecane (extra pure reagent) was used as the standard. Compositions of products determined by the GLC analysis are shown in Table 1.

Table 1. Compositions of products[a)]

θ/h	Contents/wt%			
	1	2	Diacetylmesitylene	Others[b)]
0	98.5	0	0	1.5
2	26.3	70.5	trace	4.1
4	12.0	85.1	0.4	2.5
6	6.8	89.6	0.5	3.3
8	3.8	92.9	0.6	2.8

a) At 70 °C, $C_{1,0}=0.500$ mol dm^{-3}, $C_{Ac_2O,s}=1.20$ mol dm^{-3}, $C_{AcCl,s}=0.300$ mol dm^{-3}, and $C_{FeCl_3,s}=0.100$ mol dm^{-3}. b) Isomeric trimethylbenzenes, their monoacetylated prcducts, and an unknown product are included.

Identification of the Products. From the reaction mixture, **1**, 2′,4′,6′-trimethylacetophenone(**2**), and 2,4-diacetylmesitylene were identified by means of gas chromatography-mass spectroscopy(Hitachi M-80).

Results

Rate Equation. All the acetylation runs of **1** yielded 2′,4′,6′-trimethylacetophenone (**2**) exclusively. The initial rate of the acetylation was proportional to the initial concentration of **1** and also to the sum of the starting concentrations of AcCl and Ac_2O, in the reactions with 0.1 mol dm^{-3} of $FeCl_3$, 0.5—1 mol dm^{-3} of **1**, 0.35—1.35 mol dm^{-3} of Ac_2O, and 0.15 mol dm^{-3} of AcCl at 70 °C. When HCl and Ac_2O were adopted instead of using the equivalent amount of AcCl, the rate did not change. It was estimated that AcCl was rapidly solvolyzed by AcOH to form Ac_2O and HCl, and then participated in this reaction:

$$AcCl + AcOH \rightleftharpoons Ac_2O + HCl. \tag{1}$$

Therefore, the rate is proportional to the concentration of **1** and the effective concentration of Ac_2O *in the reaction system.* The rate of the acetylation was defined as $dC_2/d\theta$ and was expressed by the 2nd order rate equation(2):

$$dC_2/d\theta = k_2C_1C_{Ac_2O} = k_2(C_{1,0}-C_2)(C_{Ac_2O,s}+C_{AcCl,s}-C_2), \tag{2}$$

where θ, C, k_2, and 0 represent the time, the concentration of the species defined by the suffix, the second order rate constant, and $\theta=0$ respectively; the suffix s represents a starting concentration defined by: {the amount of the material or the catalyst used for the reaction}×{the volume of the reaction system}$^{-1}$. When $C_{1,0}\neq C_{Ac_2O,s}+C_{AcCl,s}$, integration of Eq. 2 gives

$$\begin{aligned}&\log((C_{Ac_2O,s}+C_{AcCl,s}-C_2)/(C_{1,0}-C_2))\\&= k_2\theta(C_{Ac_2O,s}+C_{AcCl,s}-C_{1,0})\\&\quad+\log((C_{Ac_2O,s}+C_{AcCl,s})/C_{1,0}).\end{aligned} \tag{3}$$

The rate equation(2) fitted for reactions by each catalyst up to any conversion of **1** in the range of 0—90%, as illustrated by straight lines in Fig. 1. This is consistent with the above estimation that the equilibrium in Eq. 1 lies well to the right. This also indicates that the concentration of the catalytically active species does not change with the formation of **2**. Therefore, the present reaction medium avoids the deactivation of catalysts due to the complex formation[7)] between the Lewis acid and the product ketone(**2**).

Temperature Dependency of k_2. In Fig. 2, Arrhenius plots for k_2 by each catalyst are shown. The apparent activation energies are the same in all cases, *i.e.*, 18.8 kcal mol^{-1}. Therefore, relative activities of the catalysts must entirely be due to the pre-exponential factors of k_2. The constant activation energy suggests that each catalyst causes the same change of

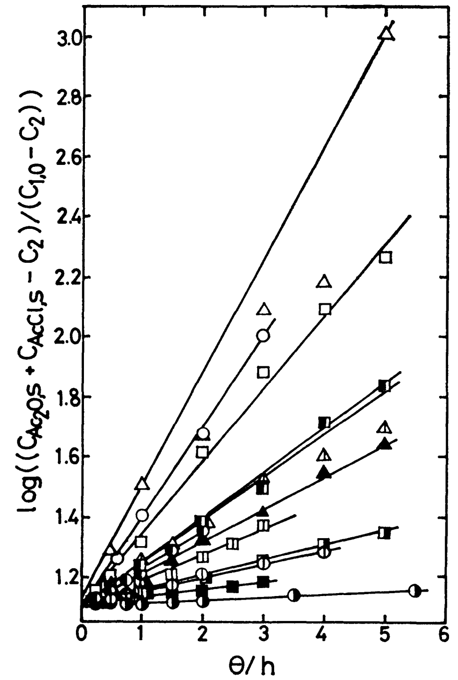

Fig. 1. Correlations between $\log((C_{Ac_2O,s}+C_{AcCl,s}-C_2)/(C_{1,0}-C_2))$, the left hand side of Eq. 3 and θ. $C_{1,0}=0.500$ mol dm^{-3}, $C_{Ac_2O,s}=1.350$ mol dm^{-3}, and $C_{AcCl_s,s}=0.150$—0.170 mol dm^{-3}. $FeCl_3$ 0.100 mol dm^{-3}, at 70 °C(○), 60 °C(◐), 50 °C(⦶), and 30 °C(◑); $SnCl_4$ 0.102 (□), 0.053 (▥), and 0.023 mol dm^{-3} (■) at 90 °C; $SnCl_4$ 0.201 (◧) and 0.101 mol dm^{-3} (◨) at 70 °C; $SbCl_5$ 0.108 (△) and 0.054 mol dm^{-3} (◬) at 70 °C; $SbCl_5$ 0.107 (▲) at 55 °C.

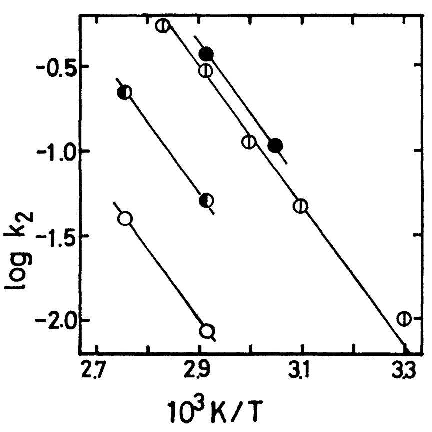

Fig. 2. Arrhenius plots of k_2 with 0.100 mol dm^{-3} of $SbCl_5$ (●), $FeCl_3$ (⦶), $SnCl_4$ (◐), and $ZnCl_2$ (○); $C_{AcCl,s}=0.150$ mol dm^{-3}.

the structure of species to form an activated complex in a rate determining step.

Dependency on the Catalyst Amount. In Fig. 3, the $\log k_2$ values are plotted against the $\log C_{\mathrm{MCl}_n,\mathrm{s}}$ of each catalyst. In the linear correlations of slope= 1—1.4, Fig. 3 shows that each k_2 is proportional to $C_{\mathrm{FeCl_3,s}}{}^{1.0}$, $C_{\mathrm{SbCl_5,s}}{}^{1.3}$, or $C_{\mathrm{SnCl_4,s}}{}^{1.4}$. The slopes of $SnCl_4$ at 70 and 90 °C are the same. The specific activity of a catalyst, k_2', was estimated by the extrapolation of the straight line to the point where $C_{\mathrm{MCl}_n,\mathrm{s}}=1\ \mathrm{mol\ dm^{-3}}$ in Fig. 3.

Effect of the Acid Strength of the Catalyst. In Fig. 4, $\log k_2'$ is plotted against the infrared spectroscopic shifts in carbonyl stretching frequencies ($\Delta\nu_{\mathrm{CO}}$) between free xanthone and its complexes with metal halides.[17] These $\Delta\nu_{\mathrm{CO}}$ values indicate the relative Lewis acid-strength of the catalysts. The correlation in Fig. 4 suggests that Lewis acid-strength is an important factor of the catalytic activity.

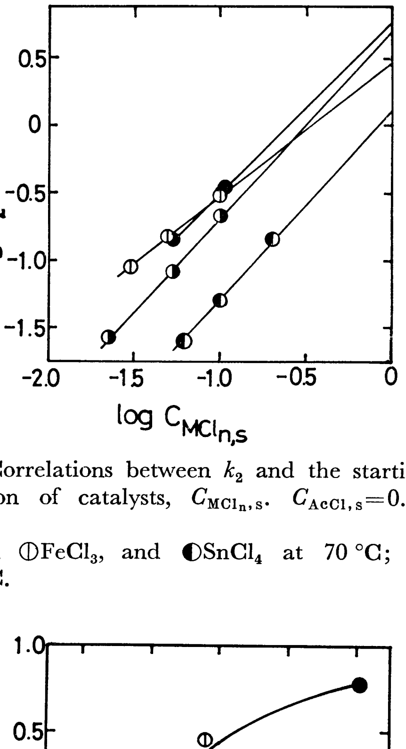

Fig. 3. Correlations between k_2 and the starting concentration of catalysts, $C_{\mathrm{MCl}_n,\mathrm{s}}$. $C_{\mathrm{AcCl,s}}=0.150\ \mathrm{mol\ dm^{-3}}$.
●$SbCl_5$, ⦶$FeCl_3$, and ◐$SnCl_4$ at 70 °C; ◑$SnCl_4$ at 90 °C.

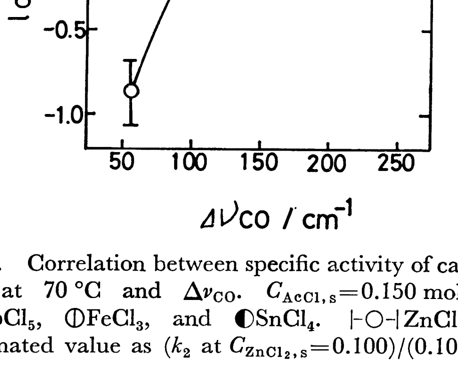

Fig. 4. Correlation between specific activity of catalysts, k_2' at 70 °C and $\Delta\nu_{\mathrm{CO}}$. $C_{\mathrm{AcCl,s}}=0.150\ \mathrm{mol\ dm^{-3}}$. ●$SbCl_5$, ⦶$FeCl_3$, and ◐$SnCl_4$. ├○┤$ZnCl_2$; the estimated value as (k_2 at $C_{\mathrm{ZnCl_2,s}}=0.100$)/($0.100^{1-1.4}$).

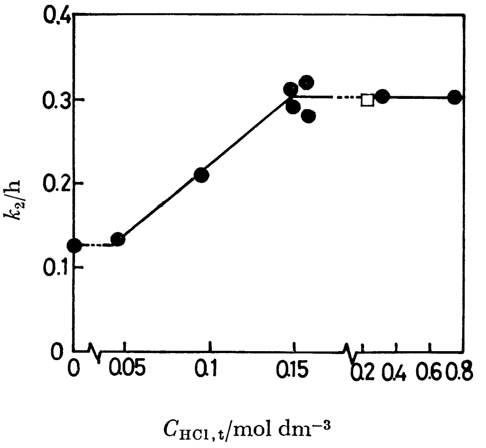

Fig. 5. Effect of C_{HCl} on k_2 of $FeCl_3$ at 70 °C. $C_{\mathrm{FeCl_3,s}}=0.100\ \mathrm{mol\ dm^{-3}}$. □$C_{\mathrm{AcCl,s}}=0$; ●$C_{\mathrm{HCl,s}}=0$.

Effect of HCl-Concentration. Figure 5 indicates the effect of C_{HCl} on the k_2 value of $FeCl_3$. The total HCl concentration was defined as the $\{C_{\mathrm{AcCl,s}}+C_{\mathrm{HCl,s}}\}$ value and was denoted by $C_{\mathrm{HCl,t}}$. In Fig. 5, k_2 values vary with the $C_{\mathrm{HCl,t}}$ value roughly along the same line. $FeCl_3$ still effected a catalytic activity when $C_{\mathrm{HCl,t}}=0$. The k_2 value appears constant in the range of $C_{\mathrm{HCl,t}}=0$—$0.05\ \mathrm{mol\ dm^{-3}}$, increases proportionally to the increase of $C_{\mathrm{HCl,t}}$ in the range from 0.05 to $0.15\ \mathrm{mol\ dm^{-3}}$, and attains approximately a maximum when $C_{\mathrm{HCl,t}}\geq 0.15\ \mathrm{mol\ dm^{-3}}$.

Figure 5 shows that the catalytic activity of $FeCl_3$ when $C_{\mathrm{HCl,t}}\approx 0.15\ \mathrm{mol\ dm^{-3}}$ is 2.4 times as high as the one in the absence of HCl.

Discussion

Co-catalytic Action of HCl and AcOH on $FeCl_3$. In Friedel-Crafts acylations, the co-catalytic effects[12] of Brönsted acid(HY) on a metal halide have not been studied. Figure 5 suggests that the co-catalytic activity of AcOH is lower than that of HCl. The activity order seems parallel to the order of the reactivities of Brönsted acids HY in their hydrogen isotope exchange with aromatic solvents in the presence of $SnCl_4$ found by Satchell:[15] namely, $HCl > H_2O > AcOH$. He explained these observations by the co-catalytic effect of HY on $SnCl_4$.

Figure 5 shows that HCl prevails as the co-catalyst when $C_{\mathrm{HCl,t}}\geq 0.15\ \mathrm{mol\ dm^{-3}}$, and that AcOH prevails when $C_{\mathrm{HCl,t}}\leq 0.05\ \mathrm{mol\ dm^{-3}}$. Details of the k_2 value should be expressable by Eq. 4. When $C_{\mathrm{FeCl_3,s}}=0.1\ \mathrm{mol\ dm^{-3}}$,

$$k_2 = 0.126(1-C_{[\mathrm{FeCl_3\cdot HCl}]}/C_{\mathrm{FeCl_3,s}}) + 0.304\, C_{[\mathrm{FeCl_3\cdot HCl}]}/C_{\mathrm{FeCl_3,s}}, \qquad (4)$$

where $[FeCl_3\cdot HCl]$ denotes the catalytically active species formed by $FeCl_3$ and HCl. The first term of the right hand side represents the co-catalytic effect of AcOH; the second term, that of HCl. If $[FeCl_3\cdot HCl]$ consists of $FeCl_3$ and HCl in the stoichiometric ratio of 1:1, and if it is formed quantitatively only when $C_{\mathrm{HCl,t}}>0.05$, then $C_{[\mathrm{FeCl_3\cdot HCl}]}$ equals the smaller value of $C_{\mathrm{FeCl_3,s}}$ or $\{C_{\mathrm{HCl,t}}-0.05\}$. Eq. 4 then agrees with the line in Fig. 5.

$HAlCl_4$ and $HAlBr_4$ are considered to be capable of being present in non-polar ternary systems of Lewis acid-catalyst/Brönsted acid-co-catalyst/solvent only when the solvent functions as a H^+-acceptor base.[12–14] If HCl and/or AcOH function(s) as co-catalyst(s) *via* the conjugate acid(s) $HFeCl_4$ and/or $HFeCl_3(OAc)$, they exist as ion pairs $AcOH_2^+FeCl_4^-$(**3**) and $AcOH_2^+$-$FeCl_3(OAc)^-$.[10a,11] This is because the present Ac_2O/AcOH–solvent system is polar and has a low dielectric constant, and the dissociation of the acid is suppressed.[18]

The equilibrium in Eq. 1 essentially lies to the left.[10b] When HCl is replaced by a strong acid such as perchloric or sulfonic acid, the equilibrium is shifted well to the right.[9,10a] Like $HAlCl_4$ and $HAlBr_4$, the conjugate acid $HFeCl_4$ formed by the interaction of Lewis and Brönsted acids presumably functions as an exceedingly strong acid and may be non-existent in the free state.[12,13] Then the observation in kinetics that the equilibrium in Eq. 1 lies well to the right can be interpreted in terms of the conjugate acid formation(5):

$$\mathrm{HCl + FeCl_3 + AcOH \overset{K_1}{\rightleftharpoons} AcOH_2^+FeCl_4^-}. \qquad (5)$$

Catalytic Action of the $FeCl_3$–HCl/AcOH System. In the results shown in Figs. 1—4, $C_{\mathrm{HCl},t}$ was 0.15—0.17, which was greater than $\{C_{\mathrm{FeCl_3},s}+0.05\}$ in every case. In those cases, k_2 of $FeCl_3$ is proportional to $C_{\mathrm{FeCl_3},s}$ but independent of $C_{\mathrm{HCl},t}$; $K_1 \gg 1$ is deduced from the analyses of Figs. 3 and 5.

According to Burton and Praill,[9] mixtures of perchloric and acetic acids which contain protons or solvated hydrogen ions, $AcOH_2^+$, are not O- or C-acetylating agents. Addition of Ac_2O to such mixtures leads to the formation of acetylium (Ac^+) and/or diacetoxyoxonium ion (Ac_2OH^+):

$$\begin{aligned}\mathrm{AcOH_2^+ + Ac_2O} &\rightleftharpoons \mathrm{Ac_2OH^+ + AcOH}\\ &\rightleftharpoons \mathrm{Ac^+ + 2AcOH}.\end{aligned}$$

These ions are both C-acetylating agents.[9] Because $C_{\mathrm{AcOH}} \gg C_{\mathrm{Ac_2O}}$ in the present medium, Ac_2OH^+ is estimated to prevail as the acetylating agent.[9,10] Therefore the acetylation in Scheme 1 is proposed; this proceeds *via* the formation of the diacetoxyoxonium ion pair(**4**):[9,10a]

$$\left.\begin{array}{ll}\mathrm{Ac_2O} + \mathbf{3} \overset{K_2}{\rightleftharpoons} \underset{(\mathbf{4})}{\mathrm{Ac_2OH^+FeCl_4^-}} + \mathrm{AcOH} & (6)\\ \mathbf{1} + \mathbf{4} \longrightarrow \mathbf{2} + \mathbf{3} & (7)\end{array}\right\}\text{Scheme 1.}$$

This mechanism, with the pre-equilibrium(6) lying to the left, accounts formally for the observed kinetics of the first order dependence on Ac_2O, as in the O-acetylation of 2-naphthol.[10a] Provided that $K_2 \ll 1$ and that Step (7) is rate-determining in Scheme 1, the 2nd order rate expression (Eq. 2) is obtained. $FeCl_3$ functions strictly catalytically, because **3** is repeatedly regenerated. The suggestion by Burton *et al.*[9] that the formation of Ac_2OH^+ should be essential to the continuous activity of the acid catalysts seems to be kinetically proved in the present study. Because $FeCl_3$ does not exist in the free state, it does not form a complex[7] with the product ketone (**2**). The present results also kinetically support the suggestion by Hartough and Kosak for the acetylation of thiophene and furan that *catalytic amounts* of Lewis acid catalyst are sufficient in the absence of the complex formation.[1]

Catalytic Actions of $SbCl_5$, $SnCl_4$, and $ZnCl_2$. The same apparent activation energy and the observed first order dependency on Ac_2O suggest that the acetylations by $SbCl_5$, $SnCl_4$, and $ZnCl_2$ will also proceed *via* a diacetoxyoxonium ion pair like **4**. It seems reasonable to postulate that $SbCl_5$, $SnCl_4$, and $ZnCl_2$ function *via* steps similar to Scheme 1, as the active complex acid catalysts: $AcOH_2^+SbCl_6^-$ and $AcOH_2^+$-$SbCl_5(OAc)^-$, $AcOH_2^+HSnCl_6^-$ and $AcOH_2^+$-$HSnCl_5(OAc)^-$, or $AcOH_2^+HZnCl_4^-$ and $AcOH_2^+$-$HZnCl_3(OAc)^-$.[10a,11]

The observations in Fig. 3 suggest that the scheme of complex acid formation is somewhat different for each MCl_n. This should be responsible for variations in the degrees of the association and the solvation of the MCl_n's, variations in the stoichiometric compositions of the complex acids, and variations in the magnitudes of the equilibrium constants for the complex acid formations. Meanwhile, the observation of Fig. 4 suggests that Lewis acid-strength of MCl_n primarily effects the ability of proton donation to Ac_2O.

Providing that an attack of Ac_2OH^+ on the aromatic nucleus is the rate-determining step, and that the variation in the overall energy barriers of steps corresponding to Steps (6—7) by different MCl_n is negligibly small, the same apparent activation energy of each catalyst will be realized.

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